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## PATENT COOPERATION TREATY

PCT



## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

## (PCT Article 36 and Rule 70)

Applicant's or agent's file reference PCT 1083-00993/1h	<b>FOR FURTHER ACTION</b>	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/EP99/08055	International filing date (day/month/year) 25/10/1999	Priority date (day/month/year) 30/10/1998
International Patent Classification (IPC) or national classification and IPC C01C1/04		
Applicant HALDOR TOPS E A/S et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 4 sheets, including this cover sheet.

- This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 2 sheets.

3. This report contains indications relating to the following items:

- I    Basis of the report
- II    Priority
- III    Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV    Lack of unity of invention
- V    Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI    Certain documents cited
- VII    Certain defects in the international application
- VIII    Certain observations on the international application

Date of submission of the demand 17/05/2000	Date of completion of this report 01.03.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized officer Zalm, W Telephone No. +31 70 340 2804
	

INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT

International application No. PCT/EP99/08055

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17.)*):

Description, pages:

1-6 as originally filed

Claims, No.:

1-8 as received on 10/11/2000 with letter of 10/11/2000

Drawings, sheets:

1/2,2/2 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- the language of publication of the international application (under Rule 48.3(b)).
- the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.
- filed together with the international application in computer readable form.
- furnished subsequently to this Authority in written form.
- furnished subsequently to this Authority in computer readable form.
- The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- the description, pages:
- the claims, Nos.:

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP99/08055

- the drawings,      sheets:
5.  This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):  
*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*
6. Additional observations, if necessary:

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

### 1. Statement

Novelty (N)	Yes:	Claims	1-8
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-8
	No:	Claims	

Industrial applicability (IA)      Yes:      Claims      1-8  
                                        No:      Claims

### 2. Citations and explanations see separate sheet

## VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:  
see separate sheet

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

---

International application No. PCT/EP99/08055

**R Item V**

**Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

The subject-matter of independent process **claim 1** and independent apparatus **claim 7** is considered to meet the requirements of Article 33(2)-(4) PCT.

**Claim 1** defines a process for the preparation of ammonia whereby the catalyst is arranged in tubes and whereby the generated heat is removed by means of a cooling agent and by conduction. The cooling agent is selected from a salt, a mixture of salts or metals having a melting point below the temperature in the reaction zone. **Claim 7** deals with an ammonia synthesis convertor and is defined by the constructional elements necessary for cooling the catalyst in the above mentioned cooling agents.

Closest prior art document DE-A-2929300 (LINDE) discloses an apparatus for the preparation of ammonia whereby catalyst containing tubes are surrounded by a cooling medium. Although according to the claims of this document any liquid can be used, the discussion of figure 2 specifies (as single example of the medium mentioned in the document) that water is used for heat absorption.

The process of **claim 1** thus differs in the materials used as cooling medium, which feature is specified in the characterising part of the claim. The process meets the requirement for inventive step since it provides alternatives for the use of water.

The apparatus of **claim 7** is new since none of the prior art documents teaches an ammonia convertor comprising tubes for transporting the cooling medium and which are positioned concentrically around tubes filled with the catalyst material.

**Re Item VII**

**Certain defects in the international application**

The application does not meet Rule 5.1(a)(ii) PCT since the document DE-A-2929300 (LINDE) is not discussed in the description as prior art.

In the claims 1 and 7 the part comprising the features which differ from the prior art are not preceded by the words (preferably) "characterised in that" (see also Rule 6.3(b)(ii) PCT).

REPLACED BY  
ART 34 AMDT

CLAIMS

1. Process for the preparation of ammonia comprising steps of

5 contacting an ammonia synthesis gas with an ammonia synthesis catalyst arranged as reaction zone in one or more catalyst tubes;

cooling the reaction zone by heat conducting relationship with a cooling agent; and

10 withdrawing an ammonia rich effluent stream from the reaction zone.

2. The process of claim 1, wherein the ammonia synthesis gas is contacted with the ammonia synthesis gas arranged in two or more reaction zones with intermediate withdrawal of an ammonia rich effluent stream between the reaction zones.

20 3. The process of claim 1, wherein the ammonia rich effluent stream is separated in a stream of unconverted ammonia synthesis gas and an ammonia product stream, the unconverted ammonia synthesis gas is recycled to the reaction zone.

25 4. The process of claim 2 and 3, wherein the separation is obtained by cooling of the effluent stream and condensation of ammonia.

30 5. The process of claim 2 and 3, wherein the separation is obtained by adsorption of ammonia contained in the effluent stream.

35 6. The process of claim 1, wherein the cooling agent is circulated within cooling tubes, each surrounding concentrically one catalyst tube.

7. The process according to anyone of the preceding claims, wherein the cooling agent is selected from salts, metals and liquids having a melting point below the temperature in the reaction zone.

5

8. The converter for the preparation of ammonia comprising at least one catalyst tube adapted to receive ammonia synthesis gas and to hold a reaction zone of ammonia synthesis catalyst; and

10

a cooling agent at shell side of the catalyst tubes.

9.  
15

The process of claim 8, further comprising at least one cooling tube concentrically surrounding the catalyst tube(s) and adapted to hold the cooling agent.

10. The converter of claim 9, wherein wall of the cooling tube(s) is designed with a lower mechanical strength than wall of the catalyst tube(s).

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/EP99/08055

the drawings,      sheets:

5.  This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)                  Yes: Claims 1-8  
                                  No: Claims

Inventive step (IS)           Yes: Claims 1-8  
                                  No: Claims

Industrial applicability (IA)   Yes: Claims 1-8  
                                  No: Claims

2. Citations and explanations  
**see separate sheet**

**VII. Certain defects in the international application**

The following defects in the form or contents of the international application have been noted:  
**see separate sheet**

**International Patent Application N . PCT/EP99/08055**  
**Applicant: HALDOR TOPSOE A/S**  
**PCT 1083 – 00989/ej**  
**November 10, 2000**

**Claims 1 to 8**

1. A process for the preparation of ammonia comprising the steps of
  - contacting an ammonia synthesis gas with an ammonia synthesis catalyst arranged as a reaction zone in one or more catalyst tubes;
  - cooling the reaction zone by a heat conducting relationship with a cooling agent; and
  - withdrawing an ammonia rich effluent stream from the reaction zone;

wherein the cooling agent is selected from salts, mixtures of salts and metals having a melting point below the temperature in the reaction zone.
2. The process of claim 1, wherein the ammonia synthesis gas is contacted with the ammonia synthesis gas arranged in two or more reaction zones with intermediate withdrawal of an ammonia rich effluent stream between the reaction zones.
3. The process of claim 1, wherein the ammonia rich effluent stream is separated in a stream of unconverted ammonia synthesis gas and an ammonia product stream, the unconverted ammonia synthesis gas is recycled to the reaction zone.
4. The process of claim 2 and 3, wherein the separation is obtained by cooling of the effluent stream and condensation of ammonia.
5. The process of claim 2 and 3, wherein the separation is obtained by adsorption of ammonia contained in the effluent stream.

6. The process of claim 1, wherein the cooling agent is circulated within cooling tubes, each surrounding concentrically one catalyst tube.
7. A converter for the preparation of ammonia comprising at least one catalyst tube adapted to receive ammonia synthesis gas and to hold a reaction zone of ammonia synthesis catalyst; and  
at least one cooling tube concentrically surrounding the at least one catalyst tube and being adapted to hold the cooling agent selected from salts, mixtures of salts and metals having a melting point below the temperature in the reaction zone.
8. The converter of claim 7, wherein the wall of the cooling tube(s) has a lower mechanical strength than the wall of the catalyst tube(s).

## PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION  
(PCT Rule 61.2)Date of mailing (day/month/year)  
14 June 2000 (14.06.00)To:  
  
Assistant Commissioner for Patents  
United States Patent and Trademark  
Office  
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Washington, D.C.20231  
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in its capacity as elected Office

International application No.  
PCT/EP99/08055Applicant's or agent's file reference  
PCT 1083-009/coInternational filing date (day/month/year)  
25 October 1999 (25.10.99)Priority date (day/month/year)  
30 October 1998 (30.10.98)

## Applicant

SPETH, Christian

1. The designated Office is hereby notified of its election made:

 in the demand filed with the International Preliminary Examining Authority on:

17 May 2000 (17.05.00)

 in a notice effecting later election filed with the International Bureau on:

2. The election
- 
- was

 was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>7</sup> : <b>C01C 1/04</b>		A1	(11) International Publication Number: <b>WO 00/26139</b>
			(43) International Publication Date: 11 May 2000 (11.05.00)
(21) International Application Number: PCT/EP99/08055		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 25 October 1999 (25.10.99)			
(30) Priority Data: PA 1998 01398 30 October 1998 (30.10.98) DK <i>30 April 2001 30 mrs</i>			
(71) Applicant (for all designated States except US): HALDOR TOPSØE A/S [DK/DK]; Nymøllevej 55, DK-2800 Lyngby (DK).		Published <i>With international search report.</i>	
(72) Inventor; and (75) Inventor/Applicant (for US only): SPETH, Christian [DK/DK]; Kirkevangen 33, DK-3540 Lyngby (DK).			
(74) Agent: GRÜNECKER, KINKELDEY, STOCKMAIR & SCHWANHÄUSER; Maximilianstrasse 58, D-80538 München (DE).			
(54) Title: PROCESS AND CONVERTER FOR THE PREPARATION OF AMMONIA			
(57) Abstract			
Process for the preparation of ammonia comprising steps of contacting an ammonia synthesis gas with an ammonia synthesis catalyst arranged as reaction zone in one or more catalyst tubes; cooling the reaction zone by heat conducting relationship with a cooling agent; and withdrawing an ammonia rich effluent stream from the reaction zone. The converter comprises at least one catalyst tube adapted to receive ammonia synthesis gas and to hold a reaction zone of ammonia synthesis catalyst and a cooling agent at the shell side of the catalyst tubes.			

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### Process and Converter for the Preparation of Ammonia

The present invention relates to the preparation of ammonia by catalytic conversion of ammonia synthesis gas.

More particularly, this invention concerns synthesis of ammonia at high conversion rates of ammonia synthesis gas in presence of an ammonia synthesis catalyst arranged in a tubular reaction zone being cooled by a cooling agent on shell side of the tubular reaction zone. Synthesis of ammonia from synthesis gas of hydrogen and nitrogen is an exothermic process and the process requires cooling to obtain high conversion rates.

Even if the concentration of hydrogen and nitrogen in the synthesis gas is close to the stoichiometric composition for ammonia formation, complete reaction to ammonia cannot be obtained by a single passage of the synthesis gas through a catalytic bed. Furthermore, due to the exothermic nature of the ammonia synthesis, increasing temperature during passage through the catalytic bed displaces the equilibrium concentration towards lower ammonia concentration. Several methods for cooling the ammonia synthesis process are known.

The usual methods for the preparation of ammonia from synthesis gas employ either indirect or direct cooling of the synthesis gas between a number of catalytic beds, wherein the ammonia synthesis passes over an ammonia synthesis catalyst.

By direct cooling, cold synthesis gas is introduced into partly reacted synthesis gas between the beds. The disadvantage of this cooling method is dilution of the partly reacted gas with unreacted gas resulting in lower ammonia concentration in the product stream from the process.

- 2 -

By the indirect cooling method, partly reacted synthesis gas is cooled by cold gas, usually fresh synthesis gas in a heat exchanger arranged between outlet and inlet of two catalyst beds.

5

It has now been found that conversion rate of ammonia synthesis gas to ammonia is much improved when cooling the synthesis gas as it proceeds through a catalytic bed of ammonia synthesis catalyst by heat transfer to a cooling agent being in continuous heat contact with the process.

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Accordingly, this invention provides a process for the preparation of ammonia comprising steps of:

15

contacting an ammonia synthesis gas with an ammonia synthesis catalyst arranged as reaction zone in one or more catalyst tubes;

20

cooling the reaction zone continuously by transferring heat from the reaction zone to a cooling agent; and

withdrawing an ammonia rich effluent stream from the reaction zone.

25

In its most general embodiment, the above process is carried out in a converter with one or more catalyst tubes arranged in a shell for retaining a cooling agent. Synthesis gas is introduced at top of the catalyst tube and passed through the reaction zone of an ammonia synthesis catalyst. Heat being developed during conversion of hydrogen and nitrogen contained in the synthesis gas to ammonia is continuously transferred through wall of the catalyst tube to the cooling medium surrounding the tube. By continuous cooling of the process, an adiabatic temperature

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increase is substantially avoided, so that the process is carried out at substantially isothermal conditions. Isothermal conversion of the synthesis gas results in higher conversion rates of the gas to ammonia than in the known 5 ammonia synthesis processes with indirect or direct cooling of partially reacted synthesis gas, where the cooled gas is contacted with the catalyst at adiabatic conditions. Having removed heat of reaction from the reaction zone, the cooling medium is continuously or periodically withdrawn from 10 the converter and externally cooled by e.g. heat exchange with water or steam and recycled to the converter by conventional means.

In a specific embodiment of the invention, the cooling 15 agent is retained in a space formed by outer wall of the catalyst tube and inner wall of a cooling tube concentrically surrounding the catalyst tube.

As an advantageous feature of the latter embodiment, shell 20 of a reactor with a number of catalyst tubes can be avoided or made from material with considerably lower mechanical strength than in the conventional ammonia converters.

Preferably, the cooling tubes surrounding the catalyst 25 tubes are designed with a lower mechanical strength than the catalyst tube. In case of catalyst tube rupture reacting gas escaping at high pressure into the cooling tubes, ventilates into a space outside the cooling tube. Thereby, the synthesis gas depressurizes outside the cooling tubes 30 and detrimental reactions of the gas with the cooling agent are avoided advantageously.

A further object of the invention is to provide a converter 35 for the preparation of ammonia by reaction of ammonia synthesis gas in presence of an ammonia synthesis catalyst and

- 4 -

cooling the reaction as it proceeds through the synthesis catalyst, the converter comprises at least one catalyst tube adapted to receive the ammonia synthesis gas and to hold a reaction zone with the ammonia synthesis catalyst, 5 which at least one catalyst tube being arranged in a container with a cooling agent, as schematically shown in the attached Fig. 1.

10 Cooling media being useful as cooling agent in the above process and reactor will be any solid or liquid having a melting or boiling point below the desired temperature in the reaction zone, including salt or mixture of salts, metals or liquids being inert at the actual process conditions. Those cooling agents include eutectic mixtures of 15 salts like mixtures of  $\text{KNO}_3$ ,  $\text{NaNO}_3$  and  $\text{NaNO}_2$  (supplied by Degussa) and eutectic mixtures of NaOH and KOH. Further eutectic salt mixtures and cooling liquids are well known in the chemical industry. The usual temperature condition in the above process will be between 300°C and 600°C. The 20 temperature of the cooling agent has to be maintained at a predetermined level within the operation temperature range by external cooling of the agent as mentioned herein before.

25 Removal of ammonia from the ammonia rich product gas being withdrawn from the catalyst tubes is further an embodiment of the invention obtained through adsorption on an adsorbent having high affinity to ammonia at high pressure, such as regeneration of the spent adsorbent is carried out 30 through depressurization of the adsorbent and recovery of ammonia rich gas similar to separation of e.g. oxygen or nitrogen in the known pressure swing adsorption processes. Furthermore, ammonia may be separated from unconverted synthesis gas by cooling and condensation of ammonia in the

ammonia rich effluent stream from the process. Unreacted synthesis gas being separated from ammonia in the product gas may then be recycled to the catalyst tube or passed to a subsequent catalyst tube for further conversion, as 5 schematically shown in Fig. 2 and Fig. 3.

#### Example

In a specific embodiment of the present invention a synthesis feed gas at a pressure of 13.8 MPa is preheated to 10 350°C and introduced to a reactor furnished with 600 reactor tubes with an inner diameter of 80.1 mm. The tubes were loaded with an upper portion of conventional iron ammonia catalyst and a lower portion of conventional ruthenium 15 ammonia catalyst. Synthesis gas is distributed to the tubes and reacted over the ammonia catalyst. The catalyst tubes are surrounded by a shell. In the space between the shell and the tubes, a salt melt is being circulated countercurrently to the gas flow direction inside the tubes and in 20 heat conducting relationship with the synthesis. Circulation of the salt melt serves to remove heat evolved from the exothermic ammonia synthesis reaction. The salt melt is introduced at 360°C into the cooling space and leaves the reactor at 420°C. The hot melt is cooled outside the reactor to 360°C in a heat exchanger, in which the heat 25 desorbed from the salt melt is used for preheating of synthesis gas. The cooled salt melt is then pumped back to the reactor. Having passed through the catalyst reacted synthesis gas, being rich in ammonia, leaves the tubes and 30 is withdrawn from the reactor. The gas is cooled by heat exchange with fresh synthesis gas.

In Table 1 below are listed the concentrations of the components in the gas stream inlet and exit the reactor as 35 obtained by the above experiment.

- 6 -

Table 1

	Inlet gas	Exit gas
	Composition (mole%):	
5	H <sub>2</sub>	73.59
	N <sub>2</sub>	25.37
	Ar	0.36
	CH <sub>4</sub>	0.68
	NH <sub>3</sub>	27.00
10	Pressure, MPa	13.4
	Temperature, °C	402
		350

The inventive process may be employed in a one through  
15 ammonia synthesis section as well as in a more conventional type ammonia synthesis loop section or in combination with similar or other ammonia converter types in more advanced ammonia synthesis loop sections e.g. comprising feed gas converters and/or purge gas converters. The ammonia product  
20 may be retrieved from the ammonia rich product gas in the synthesis section by cooling and condensation of ammonia in the ammonia rich effluent stream or absorption. The removal of ammonia may be conducted in one or more stages, between and/or after each of the reaction zones.

**CLAIMS**

1. Process for the preparation of ammonia comprising steps of

5 contacting an ammonia synthesis gas with an ammonia synthesis catalyst arranged as reaction zone in one or more catalyst tubes;

cooling the reaction zone by heat conducting relationship with a cooling agent; and

10 withdrawing an ammonia rich effluent stream from the reaction zone.

2. The process of claim 1, wherein the ammonia synthesis gas is contacted with the ammonia synthesis gas arranged in two or more reaction zones with intermediate withdrawal of an ammonia rich effluent stream between the reaction zones.

20 3. The process of claim 1, wherein the ammonia rich effluent stream is separated in a stream of unconverted ammonia synthesis gas and an ammonia product stream, the unconverted ammonia synthesis gas is recycled to the reaction zone.

25 4. The process of claim 2 and 3, wherein the separation is obtained by cooling of the effluent stream and condensation of ammonia.

30 5. The process of claim 2 and 3, wherein the separation is obtained by adsorption of ammonia contained in the effluent stream.

35 6. The process of claim 1, wherein the cooling agent is circulated within cooling tubes, each surrounding concentrically one catalyst tube.

- 8 -

7. The process according to anyone of the preceding claims, wherein the cooling agent is selected from salts, metals and liquids having a melting point below the temperature in the reaction zone.

5

8. The converter for the preparation of ammonia comprising at least one catalyst tube adapted to receive ammonia synthesis gas and to hold a reaction zone of ammonia synthesis catalyst; and

10 a cooling agent at shell side of the catalyst tubes.

9. The process of claim 8, further comprising at least one cooling tube concentrically surrounding the catalyst tube(s) and adapted to hold the cooling agent.

15

10. The converter of claim 9, wherein wall of the cooling tube(s) is designed with a lower mechanical strength than wall of the catalyst tube(s).

1/2

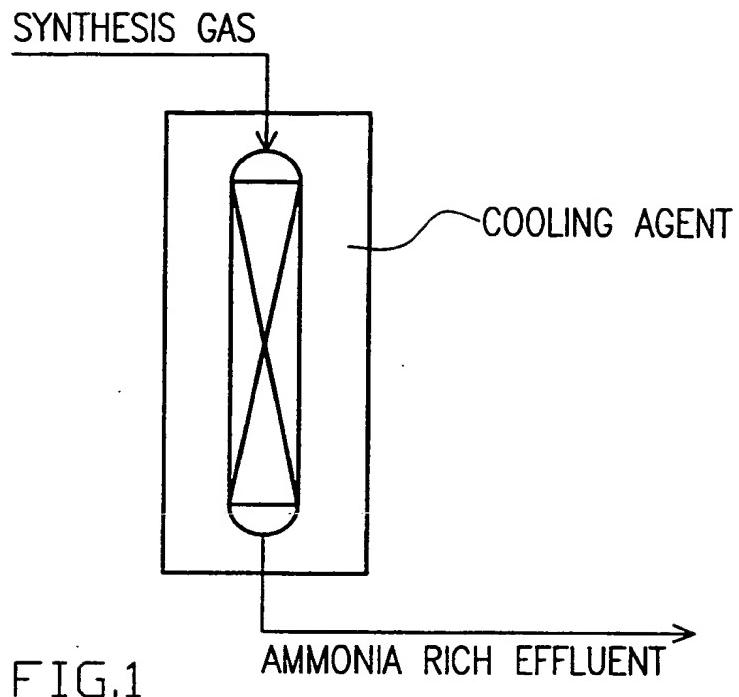


FIG.1

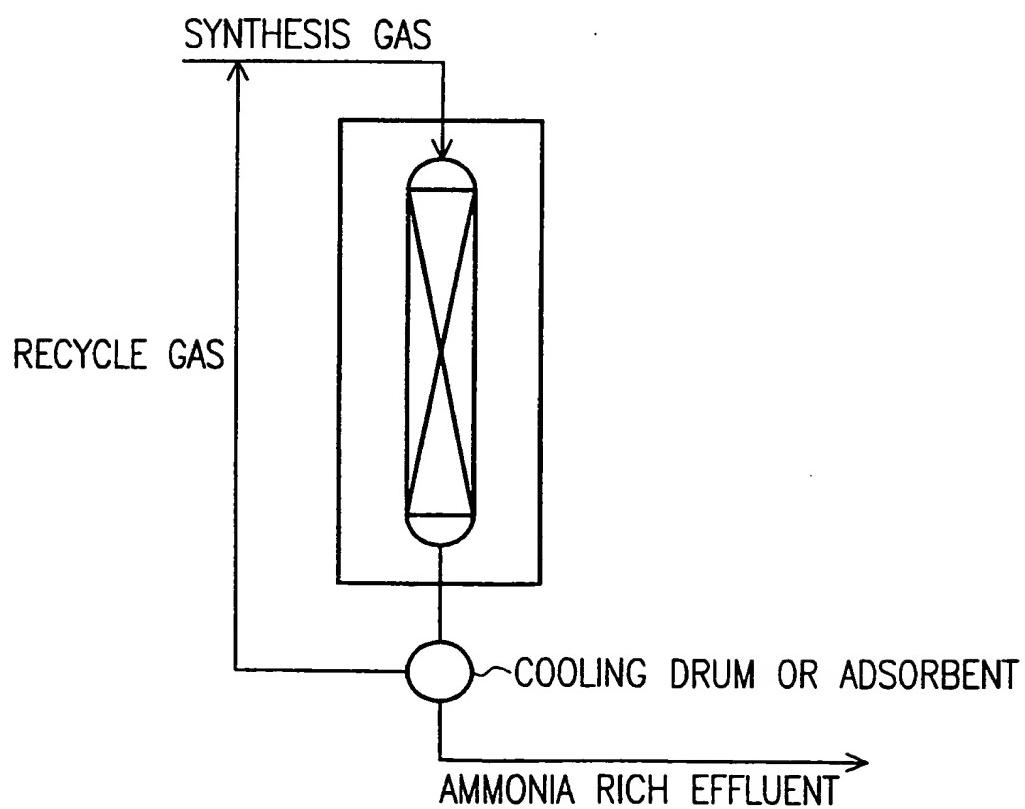


FIG.2

2/2

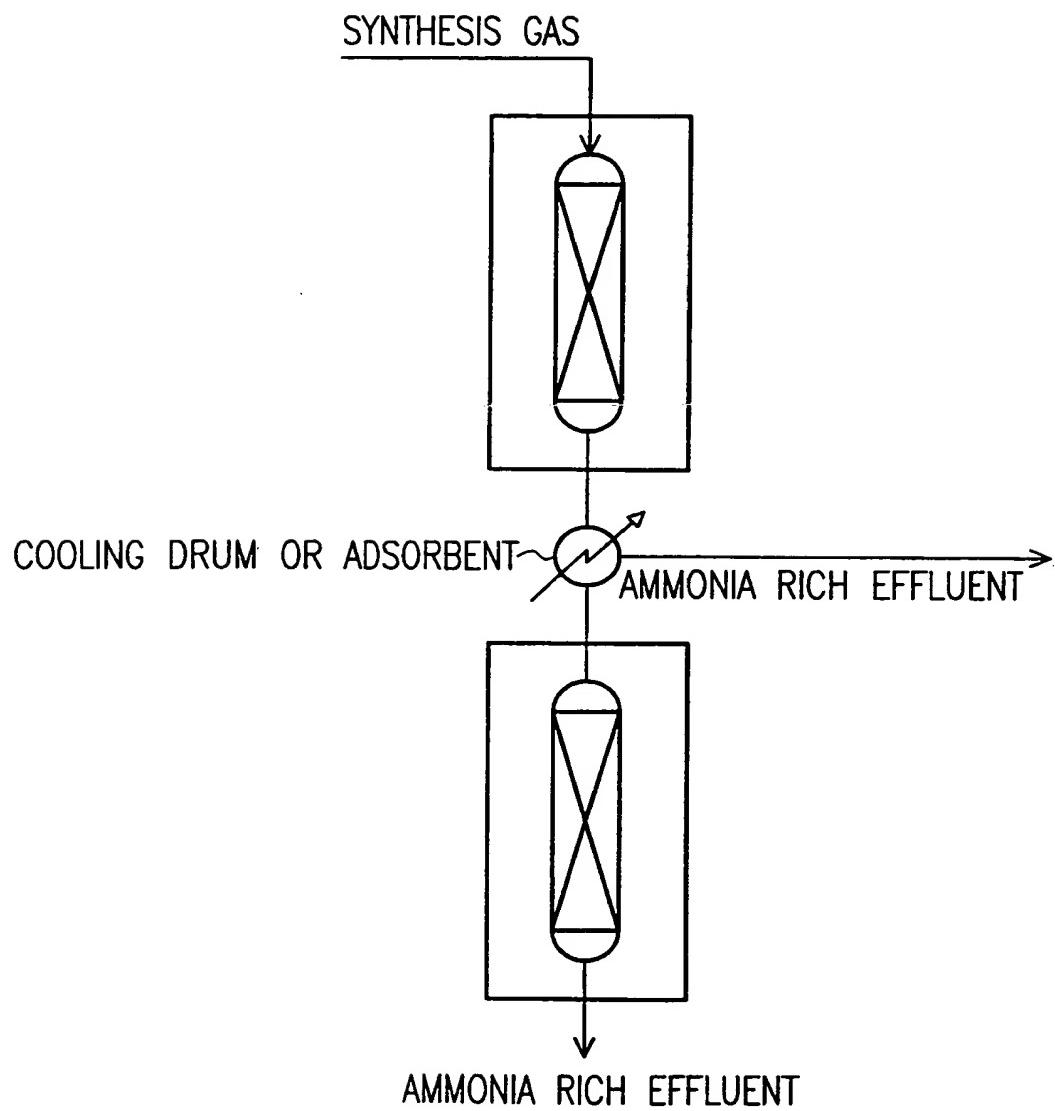


FIG.3

# INTERNATIONAL SEARCH REPORT

Inte Application No  
PCT/EP 99/08055

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01C1/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C01C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 973 995 C (METALLGESELLSCHAFT) 11 August 1960 (1960-08-11) claims; figure 2	1,4,5,7, 8
Y	---	2,3
X	DE 29 29 300 A (LINDE AG) 29 January 1981 (1981-01-29) Seite 3, Zeile 23; Seite 10, Zeile 5; Ansprüchen; Figuren	1,4,5,7, 8
Y	---	2,3
X	DE 10 66 551 B (LENTIA) 8 October 1959 (1959-10-08) claims; figure 1	1,4,5,7, 8
Y	---	2,3
	-/-	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

20 January 2000

15/02/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.  
Fax: (+31-70) 340-3016

Authorized officer

Zalm, W

## INTERNATIONAL SEARCH REPORT

Inte Application No

PCT/EP 99/08055

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	NIELSEN A. (ED.): "Ammonia catalysis and manufacture." 1995 , SPRINGER , BERLIN (DE) XP002128241 page 232 -page 237	1,4,5,7, 8
Y	---	2,3
Y	GB 1 235 565 A (TOYO ENGINEERING) 16 June 1971 (1971-06-16) the whole document	2,3
Y	---	2,3
Y	US 1 931 678 A (F. PORTER) 24 October 1933 (1933-10-24) the whole document	2,3
Y	---	2,3
	US 1 952 021 A (F. C. REED) 20 March 1934 (1934-03-20) the whole document	
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int'l Application No

PCT/EP 99/08055

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
DE 973995	C	NONE		
DE 2929300	A	29-01-1981	AT 379760 B AT 595479 A	25-02-1986 15-07-1985
DE 1066551	B	NONE		
GB 1235565	A	16-06-1971	NL 6811513 A,B, US 3615200 A	17-02-1970 26-10-1971
US 1931678	A	24-10-1933	NONE	
US 1952021	A	20-03-1934	NONE	

## PENT COOPERATION TREATY

## PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>PCT 1083-009/co</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/EP 99/08055</b>	International filing date (day/month/year) <b>25/10/1999</b>	(Earliest) Priority Date (day/month/year) <b>30/10/1998</b>
Applicant <b>HALDOR TOPSØE A/S et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 4 sheets.

It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

- the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).
- b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing :
- contained in the international application in written form.
  - filed together with the international application in computer readable form.
  - furnished subsequently to this Authority in written form.
  - furnished subsequently to this Authority in computer readable form.
  - the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
  - the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2.  Certain claims were found unsearchable (See Box I).

3.  Unity of invention is lacking (see Box II).

4. With regard to the title,

- the text is approved as submitted by the applicant.
- the text has been established by this Authority to read as follows:

5. With regard to the abstract,

- the text is approved as submitted by the applicant.
- the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No.

- as suggested by the applicant.
- because the applicant failed to suggest a figure.
- because this figure better characterizes the invention.

None of the figures.

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/EP 99/08055

**Box III TEXT OF THE ABSTRACT (Continuation of item 5 of the first sheet)**

Process for the preparation of ammonia comprising steps of contacting an ammonia synthesis gas with an ammonia synthesis catalyst arranged as reaction zone in one or more catalyst tubes; cooling the reaction zone by heat conducting relationship with a cooling agent; and withdrawing an ammonia rich effluent stream from the reaction zone. The converter comprises at least one catalyst tube adapted to receive ammonia synthesis gas and to hold a reaction zone of ammonia synthesis catalyst and a cooling agent at the shell side of the catalyst tubes.

# INTERNATIONAL SEARCH REPORT

International Application No

EP 99/08055

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7 C01C1/04

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 973 995 C (METALLGESELLSCHAFT) 11 August 1960 (1960-08-11) claims; figure 2	1, 4, 5, 7, 8
Y	---	2, 3
X	DE 29 29 300 A (LINDE AG) 29 January 1981 (1981-01-29) Seite 3, Zeile 23; Seite 10, Zeile 5; Ansprüchen; Figuren	1, 4, 5, 7, 8
Y	---	2, 3
X	DE 10 66 551 B (LENTIA) 8 October 1959 (1959-10-08) claims; figure 1	1, 4, 5, 7, 8
Y	---	2, 3
	-/-	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Y	US 1 952 021 A (F. C. REED) 20 March 1934 (1934-03-20) the whole document	2, 3
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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

EP 99/08055

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DE 2929300	A	29-01-1981	AT	379760 B 25-02-1986
			AT	595479 A 15-07-1985
DE 1066551	B	NONE		
GB 1235565	A	16-06-1971	NL	6811513 A,B, 17-02-1970
			US	3615200 A 26-10-1971
US 1931678	A	24-10-1933	NONE	
US 1952021	A	20-03-1934	NONE	